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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C22C 38/04, 38/38, 38/58 — A1

(11) International Publication Number: WO 97/03215

(43) International Publication Date: 30 January 1997 (30.01.97)

(21) International Application Number: PCT/FI96/00408

(22) International Filing Date: 11 July 1996 (11.07.96)

(30) Priority Data:

953393	11 July 1995 (11.07.95)	FI
960866	26 February 1996 (26.02.96)	FI
961922	7 May 1996 (07.05.96)	FI

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(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.
In English translation (filed in Finnish).

(54) Title: IRON-BASED SHAPE MEMORY AND VIBRATION DAMPING ALLOYS CONTAINING NITROGEN

(57) Abstract

The invention concerns a steel composition, in which, in addition to iron and manganese, there is possibly silicon, and in which nitrogen is an essential part. The composition may also include such conventional elements that are used in metallurgy to improve the desired properties. The composition contains, in addition to iron, (in percentages by weight) Mn 5.0-50.0 %, Si 0-8.0 % and N 0.01-0.8 %, as well as, if desired, one or more of the following elements: Cr 0.1-20.0 %, Ni 0.1-20.0 %, Co 0.1-20.0 %, Cu 0.1-3.0 %, V 0.1-1.0 %, Nb 0.1-1.0 %, Mo 0.1-3.0 %, C 0.001-1.0 %, rare earth metals (e.g. Sc, Y, La, Ce) 0.0005-0.02 %, and that it fulfils the following equation: $Ni + Co + 0.5Mn + 0.3Cu + 20N + 25C \geq 0.3 \times (Cr + 2Si + 5V + 1.5Nb + 1.5Mo)$. The composition has good shape memory and damping properties, as well as mechanical and corrosion resistance properties.

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Iron-based shape memory and vibration damping alloys containing nitrogen.

This invention concerns nitrogen-containing shape memory and vibration damping metals, particularly shape memory steels.

In the following text, reference is often made to only shape memory metals or shape memory steels, even though this means metals and especially steels which have both shape memory and damping properties. How great a proportion can be counted as memory properties, or correspondingly as damping properties, depends on the composition used.

Shape memory metals mean metallic materials, in which a so-called one or two-way shape memory effect appears. The shape memory effect is based on the exploitation of a martensitic transformation. When, in a one-way memory effect, an austenitic (austenite is a phase that is stable at high temperatures) sample is cooled, it forms martensite. If the formation of the martensite does not favour any direction, for example due to external stress, the shape of the piece does not change. When the material is deformed (generally less than 10 %), the twin structure of the martensite phase of the material is rearranged so that the twins that are in an advantageous orientation with the stress grow at the expense of the others and new martensite can arise as a result of the stress. When the piece is reheated above the temperature of austenite formation, the material may return to its form preceding the deformation.

In some materials, martensite does not arise during cooling, but forms during deformation. Because twinning occurs in three dimensions, the shape of the piece may even change during deformation in a very complicated manner, and nevertheless still return to its original shape when heated. A one-way shape memory effect can be exploited, for example in attachment, tensioning and prestressed structures.

When a rod-like sample deformed by straining is heated to the austenite range, the sample will recover its length before deformation, if the shape memory effect

is complete. Recovery may also be partial. If, for example, the recoverable strain is half of the strain arising from stretching, it is said that the recovery rate is 50 %. The stress caused by recovery is called recovery stress.

In a two-way shape memory effect, the material "remembers two shapes", which are achieved by heating and cooling. The temperature difference between the states may even be 1°C. Among the most important memory effect applications are so-called actuators in active vibration damping, in robotics, valves, heat relays and composite structures.

The most important memory metals used at present are Ni-Ti and Cu-based. These memory metals are quite expensive, which is the reason that the development of iron-based memory metals, i.e. memory steels, has been begun. It is possible to divide memory steels into the following classes, according to the type of lattice structure in the martensite that is obtained: BCT (Body-centred tetragonal), BCC (Body-centred cubic) and HCP (Hexagonal close-packed). In Fe-Ni-Co-Ti steel, BCT martensite is formed from the FCC (Face-centeral cubic) austenite phase. BCT martensite is generally formed in such an alloy in which there is a high stacking fault energy. A large change in specific volume is associated with the transformation. In this kind of martensite the deformation mechanism is often slip, in addition to twinning. The fact that the deformation based on slipping is non-recoverable weakens the shape memory properties of this kind of alloy. If, however, the material is alloyed in such a way that it has so-called invar properties, slip deformation is prevented, and the memory properties may be good.

In Fe-Mn-Si-based memory steels, HCP martensite arises in defomation. HCP martensite generally arises in such alloys, in which there is a small stacking-fault energy and a small change in specific volume. The memory properties are based on the fact that deformation takes place by twinning, nor does slip practically appear.

Examples of such memory steels, in which HCP martensite arises in deformation are given in US Patents 4,780,154, 4,933,027 and 4,929,289.

Th first on r ferred to is based on an iron-based alloy, composed of the following constituents:

Mn 20 - 40 % (weight %), Si 3.5 - 8.0 % and at least one of the following elements: Cr -10 %, Ni -10 %, Co -10 %, Mo -2 %, C -1 %, Al -1 %, Cu -1 %, which is balanced with iron and random impurities.

The second of the patents referred to is also an iron-based memory steel, in which there is Cr 5 - 20 %, Si 2 - 8 % and at least one of the following elements: Mn 0-1 - 14.8 %, Ni 0.1 - 20 %, Co 0.1 - 30 %, Cu 0.1 - 3 %, N 0.001 - 0.3 %, and in which Ni + 0.5Mn + 0.4Co + 0.06Cu + 0.002N $\geq$ 0.67 (Cr + 1.2Si) - 3.

The last patent referred to depicts an iron-based memory steel, in which there is Cr 0.1 - 5.0 %, Si 2.0 - 8.0 %, Mn 1.0 - 14.8 % and at least one of the following elements: Ni 0.1 - 20 %, Co 0.1 - 30 %, Cu 0.1 - 3.0 %, N 0.001 - 0.400 %, and in which Ni + 0.5Mn + 0.4Co + 0.06Cu + 0.002N $\geq$ 0.67 (Cr + 1.2Si), which is balanced with iron and random impurities.

The first of the memory steels referred to achieved a recovery rate of 75 - 90 %. The addition of at least one element from the group Cr, Ni, Co or Mo is intended to improve corrosion resistance. However, corrosion resistance is not very good in these steels, on account of the high manganese content. In addition, these alloys oxidize at high temperatures. Oxidation may occur already when the sample is being heated to the austenite range to recover the original shape after deformation. The addition of chromium to the alloy, in which there is 20 - 40 % manganese and 3.5 - 8.0 % silicon, may lead to the formation of a brittle σ-phase, which reduces the shape memory properties, formability and ductility of steel.

Also the steels according to US Patents 4,933,027 and 4,929,289 do not have good ductility values and formability characteristics. In addition, their strengths and corrosion properties are quite poor. In many cases corrosion resistance is also insufficient.

Practical applications require such memory steels that have good shape memory

properties, high strength and ductility and good corrosion resistance. They should also not oxidize at high temperatures.

On the other hand, the damping of vibration in machines, equipment and structures has become increasingly important with industrialization. Vibration causes both structural fatigue and reduces the performance of equipment. Further, vibration and noise may be detrimental to people's health. An effective way of reducing the level of vibration is to use damping materials in the manufacture of a machine causing vibration. This is often not possible, because suitable damping construction materials are not available. The iron-based damping construction materials that are most in use are grey cast irons. Their mechanical properties, above all ductility, are quite modest, which limits their use.

Certain ferrite steels have a high damping capacity. The damping is based on magneto-elasticity. Their use is limited by the fact that their damping properties are substantially weakened by deformation or welding. In addition, their strength is only at the level of mild structural steel (Fe37), and they are cold-brittle.

The phase boundary between the ε-martensite phase appearing in certain iron and manganese alloys and the austenite phase is sensitive to the mechanical loading of the material. This movement has been shown to damp vibration (C.-S. Choi et al., Proc. of the Int. Conf. on Martensitic Transformations ICOMAT-92, ed. C.M. Wayman and J. Perkins, 1993, pp. 509 - 514). The structure of the ε-martensite phase is hexagonal close-packed and that of austenite is face-centred cubic. In binary iron-based Fe-Mn alloys, the highest damping capacity is achieved with a composition Fe - 17 (mass) % Mn. This composition has been selected as the reference material for this invention.

It is the intention of this invention to create, depending on the use, either memory steels or damping steels or preferably both simultaneously, which have the aforementioned good characteristics. In other words, they have excellent shape memory properties, high strength and ductility, and good corrosion resistance, as well as high temperature oxidation resistance. The intention is to also achieve a high damping capacity. In addition, the steels should retain a high damping

capacity even when th material is cold-worked. A nitrogen alloy has a central significance in the achievement of the above properties.

The aforementioned excellent properties are achieved using steels with the characteristic features described in the accompanying Claims.

The invention is described in the following text by describing compositions according to the invention, without limiting them precisely to those described in any way whatsoever. Reference is also made to the accompanying patent drawings in which:

Figure 1(a) shows the stress-strain graphs of two example steels (curve 1 = steel number 4 and curve 2 = steel number 2) to be described later,

Figure 1(b) shows the stress-temperature graphs of the same example steels in Figure 1(a) measured during the heating cycle carried out after the treatment described. During the heating cycle, the length of the samples was kept constant. The treatments shown in the figures were carried out five times and the curves show the fifth treatment,

Figure 2 shows the length of a 6 % deformed sample of one alloy according to the invention (steel number 5) as a function of temperature,

Figure 3 shows the damping capacity (logarithmic decrement) of one steel (steel number 25) as a function of the vibration amplitude compared to the reference steel (steel number 27) and

Figure 4 shows the stress of the same steels as a function of strain.

In order for HCP martensite memory steel to have good shape memory properties, the following conditions must be fulfilled:

1. Before deformation, the amount of martensite must be as small as possible.
2. The surface energy of the stacking fault of the austenite must be as small as

possible. In addition, ε-mart nsite must form in the d formation and the quantity of α-martensit must be as small as possible.

3. The strength of the austenite must be as high as possible. In a strong matrix, the deformation of austenite through slipping becomes difficult.

4. The temperature of formation of martensite M_s must be above the Neel temperature T_N, at which antiferromagnetic ordering takes place.

There is abundant data in theory on the assumed and proven effects of various elements on the properties of memory steels. One example that can be given is the description in US Patent 4,933,027 referred to above as the state of the art, which quite extensively describes the significance of different elements in memory steels.

The aforementioned and other factors have naturally been studied in the development work on the memory steel according to the invention. On the basis of this description and of practical experiments, the contents given in the Claims were arrived at for essentially the following reasons.

1. Manganese. Manganese stabilizes austenite strongly and increases the solubility of nitrogen, which also stabilizes austenite. When the Mn-content is less than 5 %, α-martensite begins to form (in addition to ε-martensite) to such an extent that memory and damping properties begin to substantially worsen. In chromium, silicon and nitrogen-containing alloys, the reduction of the manganese content may cause the formation of δ-ferrite during the cooling following melting, which leads to the formation of porosity, because the solubility of nitrogen in δ-ferrite is very small. If, on the other hand, the manganese content exceeds 50 %, the Neel temperature rises too much, nor can even the addition of silicon and nitrogen reduce it sufficiently from the point of view of the shape memory effect.

2. Silicon. Silicon reduces the stacking fault energy of austenite, increases strength and reduces the Neel temperature. If the content is less than 2 %, the desired properties are generally no longer obtained. Nonetheless, thanks to nitrogen alloying, the memory effect is also present in such alloys in which there is no silicon at all. At silicon contents in excess of 8 %, the ductility of steels

diminishes and the hot and cold-workability is reduced.

3. Nitrogen. Nitrogen has been selected as part of the alloy, because it reinforces austenite (and martensite) more than any other element and stabilizes austenite, as well as improving corrosion resistance. Nitrogen improves both shape memory and damping properties in the alloys according to the invention. Nitrogen prevents the formation of the brittle σ-phase, which reduces ductility. An appropriate Neel temperature can be set by selecting a suitable ratio of nitrogen and manganese. The alloying of nitrogen and manganese has opposite effects on the Neel temperature. When the nitrogen content is less than 0.01 %, the effects described above are insignificant. If the content is above 0.8 %, the steel becomes brittle.

4. Chromium. The addition of chromium reduces the stacking fault energy and improves corrosion resistance and high temperature oxidation resistance. Chromium also increases the solubility of nitrogen. If the chromium content is less than 0.1 % the above effects are insignificantly small. If, on the other hand, the chromium content is above 20 %, δ-ferrite may form during the solidification stage of the smelting of the steel. In the same way, during the solidification or during the heat treatment stage of steel, brittle σ-phase may form.

5. Nickel. Nickel stabilizes austenite strongly and improves the corrosion resistance of steel and its high temperature oxidation resistance. At contents of less than 0.1 %, the effects are insignificant. At contents of more than 20 %, the temperature at which martensite still forms with the aid of deformation becomes very low, when the amount of martensite forming decreases and finally no martensite forms at all.

6. Cobalt. Cobalt improves the memory and hot-working properties of steel. At contents of less than 0.1 %, the effects are insignificantly small, while if the content grows to more than 20 %, no further improvements are gained.

7. Copper. Copper stabilizes austenite and improves corrosion resistance. The advantageous effects of copper appear, if the content is more than 0.1 %. If the copper content exceeds 3 %, the formation of ε-martensite in deformation is

prevented, because copper increases the stacking fault energy of austenite.

8. Vanadium and niobium. Vanadium and niobium increase yield strength. They also increase the solubility of nitrogen in a molten state, which is important from the point of view of manufacture. If the contents are less than 0.01 %, the effects are insignificant, while if they exceed 1 %, shape memory properties and the formability of the steel weaken. Vanadium and niobium form finely dispersed nitrides, which reinforce steel, which in turn may increase the recoverable strain of the shape memory effect.

9. Molybdenum. Molybdenum reduces the stacking fault energy and improves high temperature oxidation resistance. If the content is smaller than 0.1 %, the effects are insignificantly small, and if the content is greater than 3 %, the memory and hot-workability properties of the steel worsen.

10. Carbon. Carbon has been selected as an alloying component, because it reinforces and stabilizes austenite and improves the shape memory effect. Contents of less than 0.001 % have no effect on the properties, and if the content exceeds 1 %, ductility begins to diminish substantially.

11. Rare earth metals (e.g. Sc, Y, La, Ce). Rare earth metals prevent the precipitation of elements at the grain boundaries, which improves corrosion resistance. If the contents are less than 0.0005 %, the effects are insignificantly small. If the contents are more than 0.02 %, the mechanical properties and workability of the steel weaken decisively.

12. The ratio of the total amount of the elements stabilizing the austenite to the total amount of the elements stabilizing the ferrite.

In the steels that are the object of this invention, it is important that the material is completely austenitic, or at least that the amount of possible α-martensite is small, before deformation. Due to this, the following equation must be conformed to, in addition to the above limitations:

$$Ni + 0.5Mn + Co + 0.3Cu + 20N + 25C \geq 0.3 \times (Cr + 2Si + 5V + 1.5Nb + 1.5Mo)$$

The ability of the elements in the steel to stabilize austenite can be depicted by the nickel equivalent Ni_{equiv}, which is the left-hand side of the above equation. The right-hand side depicts the ability of the elements to stabilize ferrite, this being termed the chromium equivalent and marked Cr_{equiv}.

13. Impurities. The phosphorus and sulphur contents must be less than 0.02 %.

When all of the properties described above are taken into account, then the result according to the invention is a memory steel composition, which, in addition to iron, contains the following elements in the contents given (weight-%):

Mn 5.0 - 50.0 %, Si 0 - 8.0 % and N 0.01 - 0.80 %.

In order to improve certain properties, one or more of the following elements may be added to the composition:

Cr 0.1 - 20.0 %
Ni 0.1 - 20.0 %
Co 0.1 - 20.0 %
Cu 0.1 - 3.0 %
V 0.1 - 1.0 %
Nb 0.1 - 1.0 %
Mo 0.1 - 3.0 %
C 0.001 - 1.0 %
Rare earth metals (e.g. Sc, Y, La, Ce) 0.0005 - 0.02 %.

The following equation too should be valid:

$$Ni + Co + 0.5Mn + 0.3Cu + 20N + 25C \geq 0.3 \times (Cr + 2Si + 5V + 1.5Nb + 1.5Mo),$$

balanced with the aid of iron and random impurities.

The nitrogen alloying was observed, according to the invention, to substantially

improv not only the shape memory properties of Fe-Mn-based memory steels, but also their mechanical properties, including damping properties. Other advantages of memory and damping steels according to the invention are ease of manufacture, working and joining by welding. Because a weld also has shape memory properties, the areas of the joints do not form points of discontinuity in, for example, prestressed structures. In addition, nitrogen improves corrosion resistance and high temperature oxidation resistance. Other alloy components used in memory steel (such as Mn and Cr) increase the solubility of the nitrogen, so that the nitrogen alloying is brought sufficiently high by using the normal smelting methods used in the steel industry. By carrying out smelting in a high-pressure nitrogen atmosphere, or by using powder metallurgical manufacturing methods, it is possible to increase the nitrogen content of steel still further, but the higher cost of the manufacturing methods may then limit the applications of the steel.

The following demonstrates with the aid of examples the effect of nitrogen alloying on the properties of memory and damping steels. All of the steel examples were manufactured by conventional induction melting in an argon-nitrogen atmosphere, the partial pressure of the nitrogen being varied in order to obtain a certain nitrogen content in the alloy. After smelting, the steels were hot-rolled into 5 mm-thick bars at a temperature of 1273 - 1373 K, and then cold-drawn into 3 mm wires. When the damping properties were investigated, the steel alloys were drawn into 1 mm wires, which were annealed at a temperature of 1273 K for half an hour and then quenched in water.

Table 1 Compositions of example steels

Alloy No.	Mn	Si	Cr	Ni	V	N	Co	Cu	Nb	C
1	17.40	5.10	13.00	3.45	-	0.22				
2	16.40	5.48	8.09	3.67	-	-				
3	17.50	5.28	8.56	3.85	-	0.20				
4	18.40	5.10	9.70	3.73	0.20	0.20				

5	13.90	4.68	13.10	4.80		0.20				
6	14.90	7.60	0.20	18.00		0.04				
7	18.20	5.47	0.40			0.042	17.00			
8	16.90	2.87	8.00	12.00		0.12		2.80		
9	17.50	5.28	8.56	3.85		0.13				
10	28.80	5.24	0.20			0.11		0.20		
11	26.90	5.48	4.00	2.00		0.14				
12	24.80	5.44	5.18			0.15			0.51	
13	24.00	5.42	8.47	3.80		0.18				
14	34.30	5.87	10.10			0.39				
15	30.10	5.91	8.20	0.20	0.52	0.28				
16	40.50	5.94	12.00			0.6	0.20			
17	45.00	2.21	18.30			0.59				
18	16.00	5.20	9.10	4.30		0.14				
19	18.30	4.50	2.30	2.50	0.50	0.01				0.50
20	6.00	6.10	12.60	12.60		0.22				
21	14.00		11.60			0.23	10.00			
22	20.00	6.00	7.00			0.22		1.00		
23	20.40	5.10	9.50	3.43		0.20				
24	15.30		2.00			0.22				
25	3.70					0.20				0.004
26	15.3					0.11				0.004
27	17.5									0.005

Alloy 27 = reference alloy

Note: Alloy 18 also 1.2 Mo and 0.001 Ce; Alloys 26 - 28 also 0.001 P.

The properties of the above alloys were investigated in the manner described in the following text:

1. Mechanical properties

The yield and ultimate strengths and fracture strains are given in Table 2. The inv stigation of yield strength and fracture strains was carried out for several other

steels. The displacement rat in the testing machine fixture was 1 mm/min. The measured length of the samples was 100 mm and the thicknesses 0.8 mm.

Table 2 Yield strength (R_{002}), ultimate tensile strength (R_m) and fracture strain (R_{30}) of example steels 1 - 4

Alloy	Yield strength (MPa)	Ultimate tensile strength (Mpa)	Fracture strain (%)
1	970	1481	30
2	690	980	34
3	860	1110	32
4	850	1200	11
6	840		24
7	840		31
8	890		28
9	880		30
10	850		32
11	870		25
12	860		26
13	900		20
14	900		19
15	880		24
16	950		10
17	960		9
18	860		18
19	900		12
20	780		60
21	1020		25
22	1000		20
23	990	1280	
24	460	1080	
25	420	1000	

26	380
27	300

The nitrogen alloying was shown to increase the yield strength and ultimate strength of the steel, but it was not observed to reduce the fracture strain. Figure 4 shows stress-strain plots for materials 25 and 27 (reference alloy). Material 25 clearly work-hardens more than material 27, and the greatest value for strain measured for the nitrogen alloyed material 25 was more than 50 % greater than for the reference material 27. The test demonstrates that nitrogen alloying clearly improves precisely the mechanical properties of damping steel. The damping capacity was retained at quite a high level even in worked steel, up to a reduction of a few percent.

2. Shape memory properties

Shape memory properties were investigated on a materials testing machine using samples of 3 mm thick annealed wire, with a dimensional length of 30 mm. The samples were stretched by 5 mm and then heated above A_f temperature (at this temperature, all martensite has changed into austenite). The recovery of the strain in relation to the original strain (preceding heating) was used as a criterion of the shape memory properties. Depending on how great this value was, three quality classes were set for this ratio (shape recovery rate).

Class 1: ratio greater than 70 %
Class 2: ratio 30 - 70 %
Class 3: ratio less than 30 %

The classes of the steels are given in Table 3.

The effect of nitrogen alloying on the recovery stress was also investigated, and the results are given as graphs in Figure 1 for steels 2 and 4.

The nitrog n-alloyed sample 4 also contained Cr and V-nitrides. Figure 1 (a)

shows the increase of stress during straining. ε-martensite arises in deformation. The stress level (strength) of the nitrogen-alloyed steel 4 is clearly greater than that of steel 2, which does not contain nitrogen. The values for Fe-Mn-Si-based non-nitrogen steels given in the literature are clearly lower than those of steel 4.

Once the stress was removed, the temperature of the samples was raised to about 800 K and after that back to room temperature, keeping the strain (= length of sample) constant during the entire cycle. Stress was observed to increase at the beginning of the heating stage, because the martensite became austenite and then diminished, as a result of the thermal expansion of the sample. The maximum values for the recovery stress of steel 4 were about 300 MPa, while the value for the nitrogen-free steel 2 was only about 200 MPa. The recovery stress values given in the literature for nitrogen-free Fe-Mn-Si-based memory steels are 150 - 200 MPa.

Nitrogen-alloying thus clearly increases recovery stress. Recovery stress is a very important variable in shape memory steel applications (e.g. tighteners, fasteners and prestressed structures), often even more important than recoverable strain. The recoverable strains of nitrogen-alloyed memory steels are 1.5 - 4 %. Thermo-mechanical cycling, i.e. the so-called training of memory steel, was observed to increase the recoverable strain and to generally move the formation of austenite to a lower temperature in nitrogen-alloyed steels too. In Figure 1 (b), thermo-mechanical cycling was repeated five times and the curves of the Figure were measured from the fifth cycle. The ratio between recoverable strain and the original deformation also increased as a result of training. Its value was generally 0.6 - 1. Complete recovery was observed with a strain of as much as 3 %, for example in steel number 22.

When the temperature in Figure 1 was brought back to room temperature, a permanent stress of about 700 MPa remained in nitrogen-alloyed sample 4. In the nitrogen-free sample, the stress was less than 400 MPa. In many applications (e.g. attachments, tensioners and the prestressing of concrete), the magnitude of th- residual stress is an excellent advantage.

Nitrogen-alloyed steels according to the invention have good shape memory properties and mechanical properties, even at cryogenic temperatures. Recoverable strains of a few per cent were measured in tensile tests carried out at liquid nitrogen temperatures.

Nitrogen-alloyed shape memory steels were also observed to have a two-way shape memory phenomenon. The recoverable strain in one and two-way shape memory effect is given in Figure 2. The example steel is steel 5 of Table 1. When a sample deformed by a 6 % stretch is heated, the sample shortens by 3.5 %, which is the recoverable strain of a one-way shape memory effect. When the sample is cooled and heated after this to between -196° C - 750° C, a loop is obtained, which depicts a two-way memory phenomenon. In this steel, its magnitude is about 0.4 % after the third cycle.

3. Vibration damping properties

The damping capacities of materials 25 and 27 (reference steel) are given in Figure 3 as functions of the amplitude of the vibration. At a small amplitude with a value of 0.00005, the damping capacity (logarithmic decrement) is about 0.02. As the vibration amplitude increases, the damping capacity of both materials increases, but the damping capacity of alloy 25 increases more rapidly and at an amplitude value of 0.0002 it is more than 50 % greater than that of alloy 27. The effect of nitrogen-alloying in improving damping capacity is obvious. A high damping capacity was shown to be retained over a broad range of temperatures. The damping values of steel 26 were between those of steels 25 and 27.

The properties of shape memory and damping steels according to the invention are excellent according to all the criteria given. The values also clearly exceeded the values given in the literature.

The damping capacity (logarithmic decrement) of steels according to the invention is typically 0.01 - 0.08 at small vibration amplitudes (relative deformation 10^{-6} - 10^{-5}). At greater amplitudes, (c. 10^{-4}) the damping capacity is as much as 0.1. Steel number 23 is an example of a steel, which combines excellent mechanical

properties, corrosion resistance and memory properties (a deformation of 2.5 % is recovered completely), as well as a high damping capacity.

4. Corrosion resistance

The corrosion resistance of the steels was evaluated metallographically after the samples had been in the atmosphere for one year. The steels were divided into three classes, on the basis of the following criteria.

Class 1: No corrosion products at all observed
Class 2: Corrosion products were observed to some extent on the surface of the sample
Class 3: The surface was entirely coated with corrosion products.

Table 3 also shows the results of this test.

5. High temperature oxidation resistance

The samples were heated to 600° C in an air atmosphere and thereafter the same kind of evaluation as in Section 3 was carried out. The steels were divided into three classes on the basis of the following criteria.

Class 1: No corrosion products at all observed
Class 2: Corrosion products were observed to some extent on the surface of the sample
Class 3: The surface was entirely coated with corrosion products.

The results are given in Table 3.

Table 3 Comparison of shape memory steels according to the invention

Alloy	Shape memory property	Corrosion resistance	High temperature oxidation resistance
1	1	1	1
2	1	1	1
3	1	1	1
4	1	1	1
5	1	1	1
6	2	1	1
7	1	1	1
8	1	1	1
9	1	1	1
10	1	2	2
11	1	1	2
12	1	1	1
13	1	1	1
14	1	2	1
15	1	1	1
16	1	2	2
17	2	2	1
20	1	2	2
21	1	2	2
22	1	1	1
23	1	1	1
24	2	1	1
25	2		
26	2		
27	-	3	3

Nitrogen-alloyed memory steels according to the invention are the first shape memory materials whose properti s and prices permit the extensive industrial application of shape memory mat rials. Nitrogen-alloyed memory steels are

excellently applicable as materials for attachments (e.g. machin components, stones), tensioners (e.g. pipe connections) and various prestressed structures (e.g. concrete reinforcement steels).

The use of memory steels in the above applications is based on the fact that deformation is carried out on memory steel products before they are installed. Separate deformation is not always required, because the normal working of steel, such as the drawing of wire or the pressing, forging or cold-rolling of a plate or similar can act as the necessary deformation. This permits considerable savings in costs. During the deformation, martensite forms, the twin structure of which is oriented due to the stress field, or the twin structure of martensite that has already formed is re-oriented. After installation, the memory steel product is heated to the austenite range (typically 100 - 350°C), in which case part (or all) of the martensite changes to austenite. The product then tries to return to its pre-deformation shape, which causes the desired stress in the structure in which the product has been installed.

It should be further noted, that nitrogen-alloyed shape memory steels manufactured according to the invention have yet one more excellent property, i.e. the ability to exploit the formation of nitrides to reinforce the composition. For example, one procedure is that after cold-working the steel is aged by heating, e.g. to about 300 - 600°C. The aging causes nitrides to form and in this way the strength of the steel is further improved.

The use of shape memory steel, for example in the prestressing of concrete (or rather in prestressing that is carried out afterwards) provides construction design with quite new opportunities, because shape memory steel can be installed in the desired shape inside the mass. When the mass has hardened, the state of prestressing can be set suitably by heating the steel at a selected point, for example using induction heating or by an electric current led to the steel or other suitable manner. The use of memory steel as a prestressing method also makes it possible to increase the stress by means of heating carried out later, if the martensite phase has b en left in the steel during the first heating.

When considering purely damping properties, in this case, too, the properties and price of nitrogen alloyed steels according to the invention permit their wide industrial application. They can be used either as cast components, or as products that have been worked in various ways. They are suitable for use in large constructions too, because they can be joined by welding.

Steels according to the invention are also suitable for such applications, in which the material must absorb impact energy and shock waves (e.g. vehicles and military applications). An additional advantage of material according to the invention compared to many other metallic damping materials (e.g. Mn-Cu) is their high modulus of elasticity and high strength.

Practical tests, using memory steels according to the invention, were carried out on some applications that were regarded as suitable.

As stated above, shape memory steels are excellently suitable for many attachment and tensioning applications. Pre-deformations can be carried out at room temperature, at which it is also possible to store the deformed components (compare Ni-Ti-cryofit connectors). The moduli of elasticity of the steels are high (the moduli of elasticity of Cu and Ni-Ti-based memory metals, for example, are substantially smaller, which means that the greater part of the recoverable strain of these metals may be in elastic strain). Compared to many other memory steels, the advantages of steels according to the invention are great recovery forces and recoverable strain, high mechanical strength and ductility, good corrosion resistance and high temperature oxidation resistance, excellent steel working and machining properties. In addition, the steels can be joined by welding. The weld, too, has been shown to have a shape memory property. This can also be exploited in applications. A practical demonstration was made by bending a butt weld and straightening it by heating. Further, steels according to the invention can be economically manufactured by conventional methods used in the steel industry.

Shape memory metals according to the invention have also an excellent ability to damp shock waves and impact energy, because the deformation of austenite steel to martensite consumes a great deal of energy. In many applications, the

deformations may be very great, because the deformation mechanism is (up to a certain degree of deformation) the formation of martensite, instead of plastic deformation. Due to this, the limit of deformation of the material is very high. Applications of this include vehicle frame structures and certain military applications.

The prestressing of concrete carried out with the aid of shape memory steel was tested/demonstrated by manufacturing two reinforced steel beams (16 x 16 x 60 mm^3). Inside both beams there were four 1 mm-thick longitudinal shape memory steel reinforcements according to the invention, which were spaced at 10 mm from one another. Ties were placed round the reinforcements at intervals of about 7 mm. Separate pre-deformation was not carried out on the memory steel wires, instead normal cold-drawing of the wire to a thickness of 1 mm served as pre-deformation. The wires placed inside one of the beams were heated to a temperature of 250°C, at which most of the martensite that had arisen in the deformation changed to austenite and the wires simultaneously shortened. The wires placed inside the other beam were not heated. Both steel pillars were placed inside a form and the form was filled with concrete. The concrete was composed of normal Portland cement and sand, which was sieved through a 1.5 mm sieve. After casting, the concrete mass was vibrated to reduce voids. When the concrete beams had hardened for 6 weeks, they were heated to 250°C. A compressive stress then arose in the beam, the reinforcement wires of which had not been previously heated, as a consequence of the steel wires trying to shorten as the martensite changed to austenite. When both beams were bent, the prestressed beam broke under a greater load. This demonstrates that prestressing, carried out with the aid of shape memory steel, works.

Also the attachment of pipe connections/machine components to an axle can be carried out using shape memory steel according to the invention. Machine components, e.g. flywheels and parts of electric motors, are attached to an axle by exploiting thermal expansion. The tolerance required is achieved by either heating th machin component or by cooling th axl with e.g. liquid nitrogen. The shape memory effect can also be exploit d in attachment. The changes in dimension achieved with memory st ls are much greater than those caused by thermal

expansion. Attachment can tak place by means of e.g a sleev made from shape m mory steel. The sleeve can be pre-deformed by drawing the sleeve in the direction of the axle. When the sleeve is placed between the axle and the machine component and heating is carried out to the austenite range, the sleeve tries to return to its pre-drawing form. The thickness of its wall increases and simultaneously it tightens the machine component onto the axle. If the sleeve is made from two-way shape memory steel, the removal of the machine component takes place by cooling to a temperature that has been selected, with the aid of the alloying of the memory steel and thermomechanical treatment, so much lower than the operating temperature of the machine, that unintentional detachment cannot take place.

A pipe connection made from memory steel is a sleeve, the inner diameter of which is smaller than the outer diameter of the pipe. The inner diameter of the sleeve is enlarged to be greater than the diameter of the pipe by deforming the sleeve, e.g. by means of a mandrel. The enlarged sleeve is placed over a butt joint between two pipes. The sleeve tightens the pipes together when it is heated to the austenite range.

The attachment of a memory steel sleeve around an axle and pipe was demonstrated by manufacturing a sleeve from the memory steel to be patented, with a length of 10 mm, an internal diameter of 8 mm and a wall thickness of 2 mm. Attachment took place by heating the sleeve to 300°C. The tightening stresses were ascertained with the aid of changes in dimension.

A separate attachment component made from memory steel is not always required, because in many instances the product itself can be made from memory steel.

It is possible to exploit the invention in the attachment of a rivet, screw or other attachment member, in which a change of dimension takes place in the direction of the axle. In many attachment applications, (e.g. plates, machine components) attachment can be carried out by means of such an attachment member, which has been deformed by drawing in the direction of the axle before attachment. After installation, tightening takes place by heating the attachment member to the

austenite range. Heating can also take place in such a way that the central part of the member is heated to a higher temperature than the outer surface. In this case, more austenite arises in the inner parts than in the surface parts. A tensile stress then arises inside the member and a compressive stress in the surface. Fractures and stress corrosion do not easily arise in a surface subject to compressive stress. The exploitation of the stress gradients caused by the partial heating of memory steel is a new innovation, which can be utilized in many applications.

Construction applications demanding high resistance to fatigue can also utilize the invention. Because nitrogen-alloyed shape memory steels are strong, and they have so-called super-elastic properties, they easily withstand fatigue loadings at even high loading amplitudes. When steel is stressed, the deformation mechanism is (up to a certain limit) twinning and not slipping. This mechanism is recoverable and material fatigue is then very small. Because steels according to the invention are, in addition, cheap and easily worked and easily welded together, they are highly suitable as construction materials for large steel structures and machines in which they are subject to great fatigue loadings.

Claims

1. A shape memory and vibration damping steel composition, **characterized** in that it contains, in addition to iron, (in percentages by weight) Mn 5.0 - 50.0 %, Si 0 - 8.0 % and N 0.01 - 0.8 %, as well as, if desired, one or more of the following elements:
Cr 0.1 - 20.0 %, Ni 0.1 - 20.0 %, Co 0.1 - 20.0 %, Cu 0.1 - 3.0 %, V 0.1 - 1.0 %, Nb 0.1 - 1.0 %, Mo 0.1 - 3.0 %, C 0.001 - 1.0 %. rare earth metals (e.g. Sc, Y, La, Ce) 0.0005 - 0.02 %, and that it fulfils the following equation:
$Ni + Co + 0.5Mn + 0.3Cu + 20N + 25C \geq 0.3 \times (Cr + 2Si + 5V + 1.5Nb + 1.5Mo)$.

2. A composition according to Claim 1, **characterized** in that it contains, in addition to iron, Mn 8.0 - 45.0 %, Si 0 - 7.5 % and N 0.05 - 0.6 %, as well as, if desired, the aforementioned other elements.

3. A composition according to Claim 1, **characterized** in that it contains, in addition to iron, Mn 10.0 - 40.0 %, Si 0 - 7.0 % and N 0.1 - 0.5 %, as well as, if desired, the aforementioned other elements.

4. A composition according to Claim 1, **characterized** in that it contains, in addition to iron, Mn 13.0 - 35.0 %, Si 2.0 - 6.0 % and N 0.1 - 0.4 %, as well as, if desired, the aforementioned other elements.

5. A composition according to Claim 1, **characterized** in that it contains, in addition to iron, Mn 14.9 - 35.0 %, Si 3.0 - 6.5 %, and N 0.1 - 0.4 %, as well as, if desired, the aforementioned other elements.

6. A composition according to Claim 1, **characterized** in that it contains, in addition to iron, manganese, silicon and nitrogen, one or both of the following substances: Cr 0.1 - 20.0 % and Ni 0.1 - 20.0 %.

7. A composition according to Claim 1, **characterized** in that it contains, in addition to iron, manganes , silicon and nitrogen, one or more of the following substances: Cr 0.1 - 20.0 %, Ni 0.1 -20.0 %, Co 0.1 - 20.0 %, Cu 0.1 - 3.0 % V 0.1

- 0.8 % Nb 0.1 - 0.8 %, Re 0.0005 - 0.02 %.

8. A composition according to Claim 1, **characterized** in that it contains, in addition to iron, manganese, silicon and nitrogen, also C 0.005 - 0.6 %.

9. The use of a steel according to Claim 1 in attachments, tensioners and various prestressed structures.

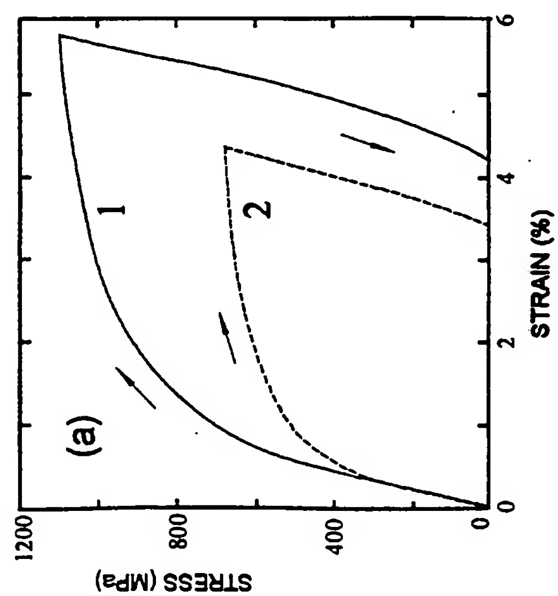
10. The use according to Claim 9 in the prestressing of concrete structures.

11. The use of a steel according to Claim 1, on account of the two-way memory phenomenon, to produce movement or force in actuator applications.

12. The use of a steel according to Claim 1 in objects requiring vibration damping.

13. The use of a steel according to Claim 1 in objects requiring the damping of impact loadings and shock waves.

14. The use of a steel according to Claim 1 in objects requiring high fatigue resistance.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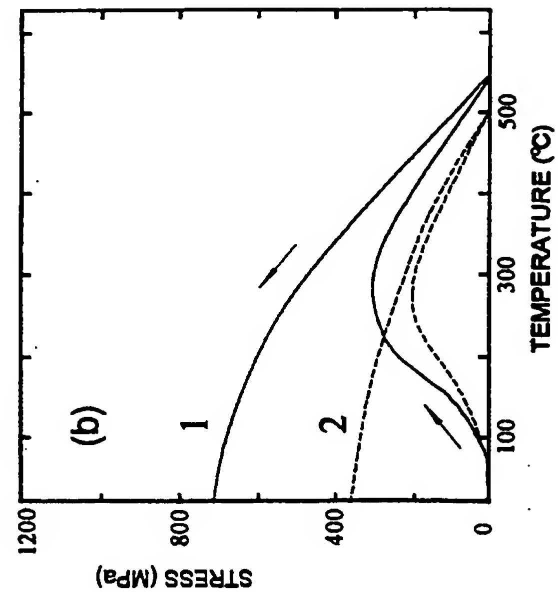
1200
0
2
4
6

F I G. 1 (a)


(b)
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TEMPERATURE (°C)
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800
1200
100
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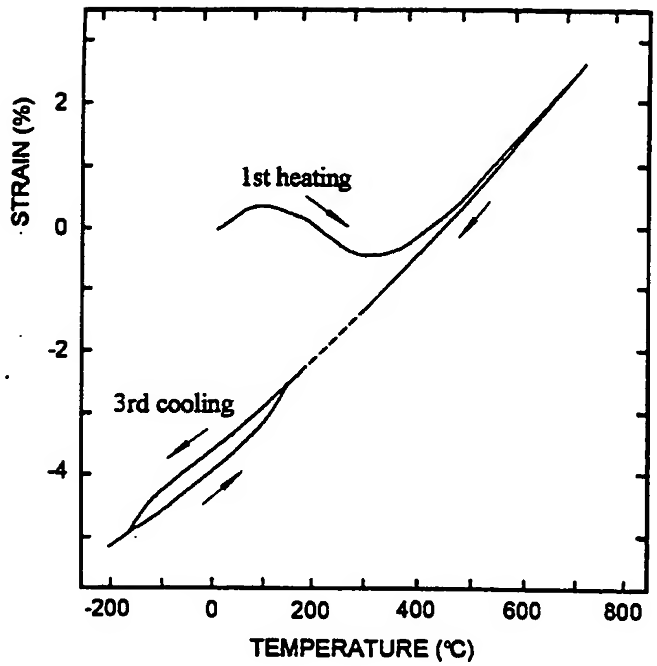
F I G. 1 (b)


STRAIN (%)
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-2
-4
1st heating
3rd cooling
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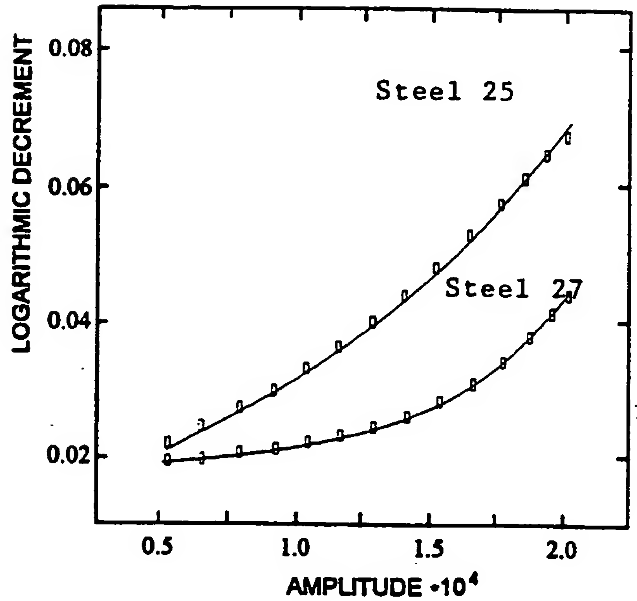
0
200
400
600
800
TEMPERATURE (°C)

F I G. 2


LOGARITHMIC DECREMENT
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0.06
0.04
0.02
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Steel 27
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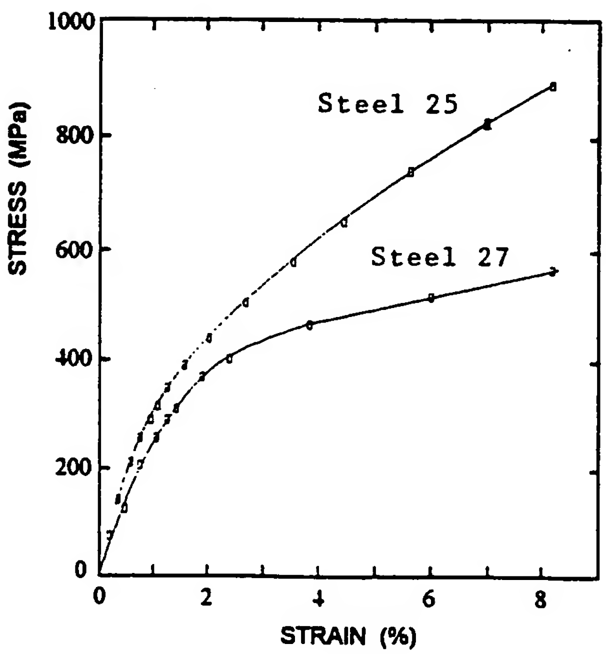
1.0
1.5
2.0
AMPLITUDE $\cdot 10^4$

F I G. 3


STRESS (MPa)
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800
600
400
200
0
Steel 25
Steel 27
0
2
4
6
8
STRAIN (%)

F I G. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 96/00408

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C22C 38/04, C22C 38/38, C22C 38/58
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

ORBIT: JAPIO, WPAT; STN: REGISTRY

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0480033 A1 (NISSHIN STEEL CO., LTD.), 15 April 1992 (15.04.92), Table 1, steels A8 and A9 --	1-14
X	JP, A, 2-301514 (NISSHIN STEEL CO LTD) 13 December 1990, Table 1, steels A8,A9 and A11 & Patent Abstracts of Japan Vol. 15, No 76, (C-809), abstract of JP 2-301514, publ. 90-12-13 --	1-14
X	EP 0489160 A1 (NISSHIN STEEL CO., LTD.), 10 June 1992 (10.06.92), Table 1, steel A9 --	1-14

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" ertier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 November 1996	14.11.1996

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 96/00408

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5173131 A (MARC MANTEL), 22 December 1992 (22.12.92), Table 1, ingots 6-8 --	1-7,9-14
X	US 4929289 A (YUTAKA MORIYA ET AL), 29 May 1990 (29.05.90), Table 1, steel 11 --	1-3,6-7,9-14
X	JP, A, 02-228451 (NIPPON STEEL CORP) 11 September 1990, Table 1, Steels 3 and 14, Patent Abstracts of Japan Vol. 14, No 539, (C-782), abstract of JP 02-228451 publ. 90-09-11 --	1-3,6-7,9-14
X	US 4933027 A (YUTAKA MORIYA ET AL), 12 June 1990 (12.06.90), Table 1, steel 12 -- --------	1,6-7,9-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

28/10/96

International application No.
PCT/FI 96/00408

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP-A1-	0480033	15/04/92	DE-D,T-	69018824	23/11/95
			JP-A-	3028319	06/02/91
			US-A-	5265919	30/11/93
			WO-A-	9100372	10/01/91
EP-A1-	0489160	10/06/92	DE-D,T-	69014126	14/06/95
			JP-A-	3082741	08/04/91
			US-A-	5198041	30/03/93
			WO-A-	9102827	07/03/91
US-A-	5173131	22/12/92	CA-A-	2030501	23/05/91
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			SE-T3-	0430754	
			ES-T-	2051487	16/06/94
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			DE-U-	6890249	24/09/92
			EP-A,B-	0336157	11/10/89
			SE-T3-	0336157	
			JP-A-	2030734	01/02/90
			SU-A-	1826994	07/07/93
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			EP-A,B-	0336175	11/10/89
			SE-T3-	0336175	
			JP-C-	1855272	07/07/94
			JP-A-	2077554	16/03/90
			SU-A-	1741611	15/06/92
			DE-U-	6890225	03/09/92